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Short communication

Absorption behavior of vanadium in Nafion®

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HIGHLIGHTS

- We study the absorption behavior of vanadium in Nafion® and conductivity loss.
- The maximum loss of IEC is measured to be less than 32% for all vanadium.
- Steric hindrance of the associated water complex may explain the lower absorption.
- Highest affinity for lowest valence and lowest affinity for highest valence.
- Vanadium exchanged NRE211s show 2–3× lower than sodium exchanged membranes.

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ABSTRACT

The absorption of vanadium to Nafion® was investigated through *ex-situ* isotherm and conductivity measurements at 23 °C. The data show a maximum loss of ion exchange capacity (IEC) of 30% for all four oxidation states of vanadium. The affinity of vanadium for N115 was measured by back titration and atomic absorption (AA) and characterized by isotherms at 23 °C, and the affinity is highest for the divalent species and lowest for the pentavalent species in the following order: VO_2^+ (V^{5+}) < VO^{2+} (V^{4+}) < V^{3+} < V^{2+}. Steric hindrance from the associated water complex may explain the lower absorption of vanadium compared to alkali metals. The conductivity for the VO^{2+} (minimum affinity)-exchanged membrane was 2–3× lower than the sodium-exchanged membrane at an approximate RH = 100%.

1. Introduction

The vanadium redox flow battery (VRFB) has been regarded as a promising large-scale energy storage device. V^{2+}/V^{3+} and V^{4+}/V^{5+} are used as the negative and positive electrolytes, respectively, in 2–5 M H_2SO_4 solutions in VRFB applications. Vanadium is present in both the positive and negative electrolytes, but the vanadium species have different oxidation states. The VRB redox reaction during the charge and discharge of the VRFB is shown as Eqs. (1) and (2) below. As in most flow batteries, the main role of a separator in the VRFB is to prevent cross-over between the negative and positive electrolytes, which decreases the open circuit voltage, increases coulombic losses and causes a mix-potential that reduces the performance of the VRFB (self-discharge) [1–8].

Discharge

$$+\,\text{electrode}: VO_2^+\left(V^{5+}\right) + 2H^+ + e^- \rightarrow VO^{2+}\left(V^{4+}\right) + H_2O,\, E^0 = +1.00\text{V vs. SHE} \quad -\,\text{electrode}: V^{2+} \rightarrow V^{3+} + e^-,\ E^0 = -0.26\text{V vs. SHE} \tag{1}$$

Charge

$$+\,\text{electrode}: VO^{2+}\left(V^{4+}\right) \rightarrow VO_2^+\left(V^{5+}\right) + 2H^+ + e^-,\ E^0 = +1.00\text{V vs. SHE} \quad -\,\text{electrode}: V^{3+} + e^- \rightarrow V^{2+},\ E^0 = -0.26\text{V vs. SHE} \tag{2}$$

Nafion®, a perfluorinated membrane that has a sulfonic acid moiety as an end group, has been used as a separator for proton exchange membrane fuel cells (PEMFCs) and Na^+ in Cl_2/NaOH electrolysis. This material has also been used in VRFB applications

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to fulfill requirements such as proton conductivity at high hydration and low permeability, while providing good mechanical, thermal, and chemical resistivity. The purpose of this paper is to present data that illustrate the isotherms and conductivity of Nafion® that has been exposed to vanadium solutions. These isotherms will provide insight for intrinsic conductivity loss of the membrane by only the selection of molar composition of vanadium and acid solutions without or/and with operating the cells.

According to contamination studies in PEMFCs, metal cations showed higher affinity to the sulfonic acid sites of the Nafion® membrane relative to protons [9–14]. Metal cations can replace acid proton sites via an ion–exchange reaction, which is an interaction between the sulfonic acid group and metal cation, resulting in conductivity and performance loss. However, many electrolytes used in flow battery systems are transient metal cations in strong acid solutions. Relatively few studies have considered the ion exchange behavior of the Nafion® membrane with transition metals. These few studies are in sharp contrast to the large volume of studies on the absorption of alkali and alkali earth metal cations [9–12] to Nafion® membranes. For transition metals, Kelly et al. [13,14] reported the absorption of transition metals such as Ni^{2+}, Cu^{2+}, and Fe^{3+} without using isotherms and did not report a conductivity loss of a N117 membrane. Li et al. [15] studied a single cell PEMFC with Co^{2+} contamination resulting from a bimetallic catalyst *in-situ*. Additionally, a number of studies [9,16–22] of vanadium ions were conducted to check the durability of Nafion® membranes using the metrics membrane resistance change, ion exchange capacity (IEC) change, and vanadium ion diffusivity change [18,19]. Here we expand the data for the four valences of vanadium by presenting and comparing these isotherms with the isotherms of Na^+ and Ca^{2+}. The data are most useful at RH = 100% for flow batteries and at RH<100% for gas phase batteries or PEMFCs.

2. Experimental

2.1. Membrane isotherms for vanadium

As received VCl_2 (s), V_2O_3 (s), $VOSO_4$ (aq), and V_2O_5 (s) (Sigma–Aldrich, Saint-Louis, MO 63103, USA) were used for preparation of each vanadium ion solution by mixing with de-aerated Ar gas purged in 2–5 M sulfuric acid solutions at room temperature. The solution pH values were adjusted by changing the H_2SO_4 concentration to maintain the thermodynamic stable state: VO_2^+ (pH $\leq$ 1.45), VO^{2+} (pH $\leq$ 4.97), V^{3+} (pH $\leq$ 2.92), and V^{2+} (pH $\leq$ 2.92). These pH values were obtained by consulting Refs. [24–26] for the diagram of the predominant dissolved species in the V–H_2O. Several mixtures of sulfuric acid solution and vanadium solutions were prepared with the different molar ratios for the measurement of the absorption isotherm in a N115 membrane at 23 °C [27]. The concentrations and pH values of V_2O_5, $VOSO_4$, V_2O_3, VCl_2, and H_2SO_4 are shown in Appendix A.

The isotherm experiments included a membrane pretreatment step, followed by immersion of the membrane in the vanadium solution of interest, then extraction of the vanadium from the membrane, and concluded with digestion of the membrane to determine the efficiency of the extraction process.

In the pretreatment procedure, one piece of dry N115 (3.0x3.0 cm^2)[1] was used, which was weighed to calculate the IEC before being boiled in 2 M H_2SO_4 for 1 h and stored in DI water. The pretreated N115 pieces were immersed in each of the mixtures in Table A1, and magnetic stirrer plates were used to mix the samples for 48 h to allow the absorption/ion–exchange reaction between the vanadium cations and the proton form of the membrane to equilibrate. Solution concentrations before and after the immersion were measured as discussed below. To confirm the amount of vanadium that was exchanged, the membranes were placed in 2 M H_2SO_4 to extract the previously exchanged vanadium. Finally, after extraction the membranes were digested with 10 ml of a concentrated 1:1 mixture of HCl and HNO_3 in a 900 W microwave for 2 min.

The concentration of the vanadium ions in the solutions used for immersion was measured with an atomic absorption spectrometry (AA) instrument and a UV–vis. spectrophotometer. For the UV–vis., 250 nm was chosen as the wavelength for the quantification of vanadium ions. The calibration curve of the UV–vis. intensity measurement was linear at 250 nm for concentrations of vanadium solutions ranging from 0.05 to 5 mM with an accuracy of $\geq \pm 0.05$ mM. The purpose of the digestion step was to confirm that no residual vanadium ions were in the Nafion® membrane after the acid extraction. The digested solutions were analyzed by ion chromatography inductively coupled plasma (ICP) mass spectrometry and all the reported data showed that the residual vanadium was less than 0.03 ppm in the digested solutions.

2.2. Membrane conductivity measurement

For the conductivity measurements, NRE211 was used to minimize the time to reach equilibrium. Membrane conductivities for pristine and vanadium absorbed[2] NRE211 were determined at 10 values of constant relative humidity (RH) (i.e., 10, 20, 30, 40, 50, 60, 70, 80, 90, 95%) by applying DC currents at the cell temperature of 80 °C. The potentiostat (model PAR273) was used with a four-probe conductivity Teflon-based cell (model BT-112) made by Beckktech LLC. The cell was equilibrated with a 300-sccm flow of N_2 at T_{cell} = 80 °C and RH = 90% for 1 h using a Scribner 890E PEMFC test station that was calibrated for both flow and humidity. The humidity was changed from low (20%) RH to high (95%) RH while the membrane conductivity was measured with a hold of 30 min for each RH to ensure equilibrium conditions.

A VAISALA dew point chamber was attached at the outlet of the conductivity cell to confirm the dew point temperature of outgases relative to those temperatures set by the test station. We verified that the degree of absorption did not change during the conductivity measurements by the digestion protocol described above.

3. Result and discussion

3.1. Absorption isotherm of vanadium ions into Nafion® membrane

Fig. 1 shows absorption isotherms of N115 for different oxidation states of vanadium ions at room temperature. The results show that for all the range of vanadium ions, exchange was 5–32% of the acid sites in N115. The total number of acid sites was measured with batch titration methods using Na^+ (e.g., 0.98 ± 0.05 meq g^{-1}) [23] (i.e., available acid sites 0.9 meq g^{-1} minimum and total capacity is 0.9–1.0 meq g^{-1}). The maximum exchange ratios for each of the vanadium ions were VO_2^+ = 3%, VO^{2+} = 12%, V^{3+} = 29%, and V^{2+} = 34% with regard to IEC. For example, the IEC for N115 VO^{2+} was 0.15 ± 0.05 meq g^{-1} when measured by extraction as described

[1] Note that these results measured for N115 can be representative for different Nafion® PFSA membranes as well due to the same chemical structure, available acid sites, and conductivity (i.e., EW = 1100 g $equiv^{-1}$).

[2] We use 'absorbed' interchangeably with 'partial ion exchange' to describe the uptake of vanadium. Note that the measurement of % exchanged did not change during the conductivity measurement.

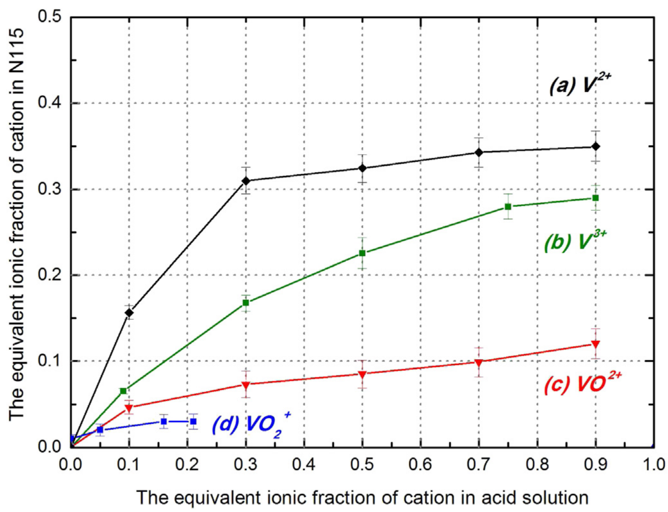

Fig. 1. Absorption isotherm curves of vanadium ions for Nafion®.

above, whereas the value when measured with Na^+ was 0.98 ± 0.05 meq g^{-1}. Note that these affinity values of the vanadium ions for Nafion® are greater for the lower valence species than the higher valence species. This affinity is an initial value and could change over extended periods of time when Nafion®, Gore Select, and Selemion are immersed in 0.1 M VO_2^+ (V^{5+}), as described in Ref. 17 and 18. Additionally, the isotherms exhibit greater affinity to N115 in the reverse order of the valences of the vanadium ions: VO_2^+ (V^{5+}) < VO^{2+} (V^{4+}) < V^{3+} < V^{2+}. All the results were obtained after soaking N115 for 2 days in the vanadium and sulfuric acid solution. Note that previous studies [16,17] reported that the membrane IEC may change after the Nafion®, Gore-Select, and Selemion membranes are immersed in a 0.1 M V^{5+} and sulfuric acid solution due to membrane swelling as a result of membrane dissolution. Note that it is possible to change of IEC based on volume of dry and/or wet membrane (meq g^{-3}). However, the IEC based on weight (meq g^{-1}) is not changed. Here, we use 'IEC' based on weight (meq g^{-1}) thoroughly in this paper.

The contrast between sodium and vanadium ion exchange could be a resulting of the Donnan equilibrium potential [27], which explains the electric potential difference between the membrane and solution. This perspective would argue that the concentration in the VRFB (i.e., 2–5 M electrolyte) precluded or minimized the ion exchange or absorption of vanadium ions in Nafion®. Thus, a higher concentration of vanadium would have a lower maximum% exchange. This concentration effect (i.e., an increase in the exclusion of electrolytes with an increase of the external solution concentration) was not observed for V^{3+}, as shown in Fig. 2(a). The Donnan potential effect on an ion is proportional to the ionic charge number, so a higher valence cation (i.e., V^{5+}) is more strongly repulsed by the membrane. For example with alkali metals, the Ca^{2+} isotherm curves for Nafion® decreased as the concentration increased, in contrast to the Na^+ isotherm curves shown in Fig. 2(b) [23,27]. Thus, the higher solution concentrations of vanadium used in these experiments (up to 3.6 M shown in Appendix A1) compared to Na^+ concentrations (0.1 M) in this experiment may increase the Donnan potential between the membrane and vanadium solution. The Donnan potential effect on vanadium ions may explain the order of the affinities observed for vanadium ions absorbed to Nafion®. Fig. 2(a) shows that the following trend for the affinity of N115 was observed: V^{3+} (2 M H_2SO_4) < V^{3+} (0.1 M H_2SO_4) < V^{3+} (0.05 M H_2SO_4), but this change is not significant. Additionally, the maximum % exchange for V^{3+} at different concentrations was equal to approximately 0.3 (Table 1).

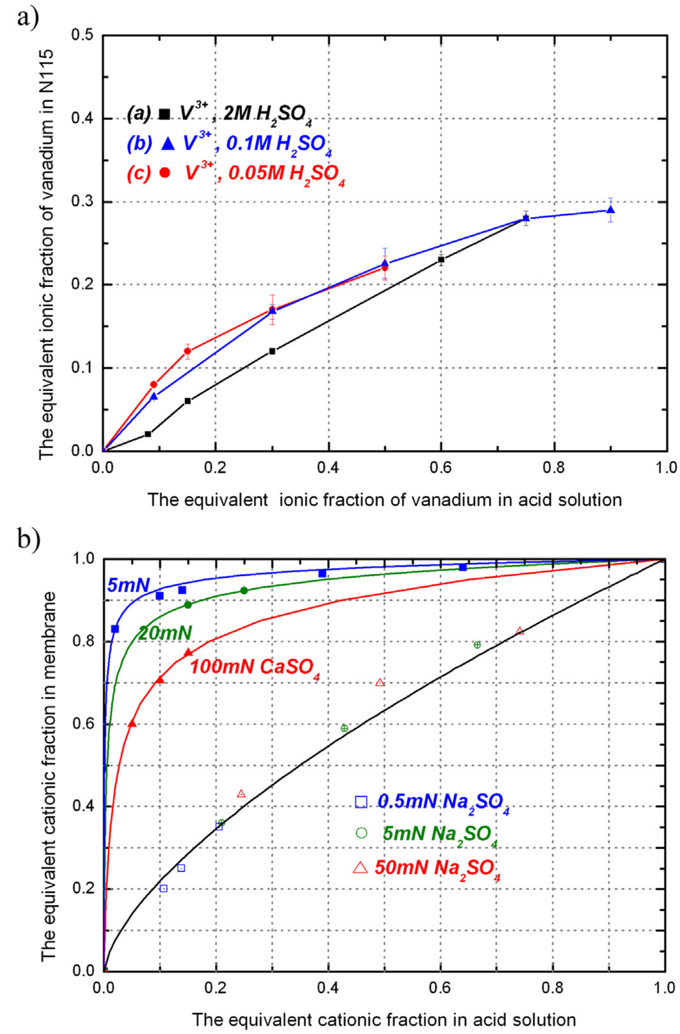

Fig. 2. Comparison of absorption isotherm curves of Nafion® with VO^{2+} (V^{4+}) in different concentration of H_2SO_4 solutions compared to Na^+ and Ca^{2+}.

The lower% exchange by vanadium may also be explained by a sieve or steric effect. Thus, the size of the complex would affect the % exchange by vanadium. We would expect a change in size because transition metals form covalent bonds with water in aqueous solutions [24–26]. The lone electron pairs of water molecules are shared with the empty 3d, 4s, and 4p orbitals of the transition metal. The hydrolysis products of the vanadium ions in acid solution are listed in Table 2, which show that the aqueous vanadium ions are hexagonally oriented in an octahedral shape in

Table 1
Comparison of absorption isotherm curves of Nafion® with VO^{2+} (V^{4+}) in H_2SO_4 solutions with different concentration.

V^{3+} in H_2SO_4					
0.05 M H_2SO_4		0.1 M H_2SO_4		2 M H_2SO_4	
X in solution	X in N115	X in solution	X in N115	X in solution	X in N115
0.00	0.00	0.00	0.00	0.00	0.00
0.09	0.08	0.09	0.07	0.08	0.02
0.15	0.12	0.30	0.17	0.15	0.06
0.30	0.17	0.50	0.23	0.30	0.12
0.50	0.22	0.75	0.28	0.60	0.23
		0.90	0.29	0.75	0.28

X: The equivalent ionic fraction of vanadium (vanadium vs. proton).

Table 2
Vanadium ion form in the acid solution (octahedral shape).

Vanadium	Hydrolysis product	Remark
V^{2+}	$[V(H_2O)_6]^{2+}$	Black, inert, slow kinetics
V^{3+}	$[V(H_2O)_6]^{3+}$	Black, blue aqua ion
VO^{2+}	$[VO(H_2O)_4]^{2+}$, $[VO(H_2O)_5]^{2+}$	Blue aqua ion
VO_2^+	$[VO_2(H_2O)_4]^+$	Pale yellow, colloidal materials

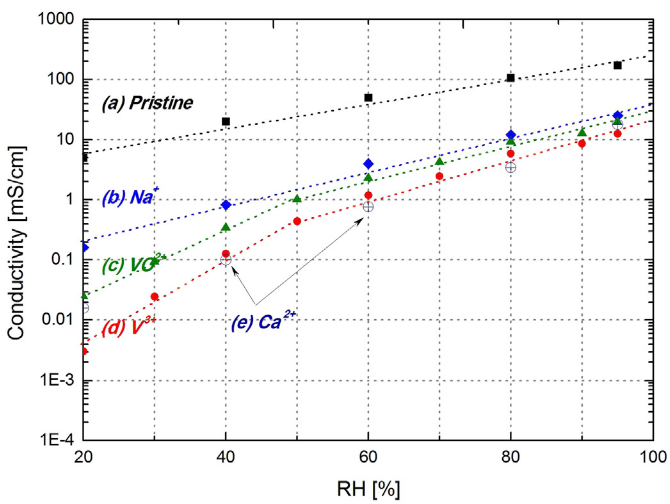

Fig. 3. Comparison of membrane conductivity of Nafion® with $VO^{2+}(V^{4+})$, V^{3+}, Na^+, and Ca^{2+}.

the acid solution [24,25]. These ligands must associate with the hydrophilic ionic clusters (ca. 5 nm dia.) of the water channels in a Nafion® membrane, which were reported to be 1 nm as measured using a small angle X-ray spectrometer (SAXS) [28]. Thus, a size exclusion or sieve effect can occur for the vanadium hydrolysis complex, and these complexes support the smaller % absorption of vanadium observed in Fig. 1.

From a practical perspective, the isotherm curves can be used to provide a concentration of vanadium ions in a Nafion® membrane. For example, the loss of acid sites should be less than 10% by VO_2^+ (V^{5+}) at the open circuit voltage (OCV) as shown in (d) of Fig. 1. Also, the 10% and 30% of acid sites could exchange for V^{4+}/V^{5+} and V^{2+}/V^{3+} ions for electrolytes that have a molar ratio of 0.5 of vanadium ions and acid (i.e., proton) on the positive and negative electrolytes respectively (e.g., 2 M $(VO)SO_4$ + 2 M H_2SO_4). Thus, it will lead to cause the intrinsic membrane conductivity loss. During discharge or/and charge, vanadium ions on negative electrolytes (i.e., V^{2+}/V^{3+}) can be predominant ions in the Nafion® membrane due to their higher affinities for membrane. Furthermore, the quantitative analysis of conductivity loss for vanadium exchanged Nafion® membranes can obtain according to conductivity changes as a function of coverage (i.e., acid sites change by the absorption).

3.2. *The ex-situ membrane conductivity measurement*

Fig. 3 compares the conductivity for VO^{2+} and V^{3+} with Na^+ and Ca^{2+} absorbed (or exchanged) in NRE211. Interestingly, although the % absorbed for V^{3+} (i.e., 21%) was less than the value for Ca^{2+} (i.e., 60%), the conductivities of these ions were approximately the same order of magnitude for 40% < RH < 93%.

Similarly, the conductivities for Na^+ and VO_2+ were the same order of magnitude even though Na^+ occupies many more sites than VO^{2+} (V^{4+}) (i.e., 100% and 12% for Na^+ and VO^{2+}, respectively). This high conductivity loss for less % exchanged is most likely attributed to the formation of the vanadium–water complex ion. The large size of these complex ions may be accompanied by the exclusion of water from the Nafion® membrane. This excluded water has been explained by comparing the properties of alkali metal cations with sodium (smaller radius, larger hydrated radius) and potassium (larger radius, smaller hydrated radius) exchanged Nafion® membranes also showed the size effect on conductivity loss. A greater conductivity loss for the potassium-exchange membrane was observed for the same exchanged concentration compared to the sodium exchanged membrane [29]. However, the greater conductivity loss for V^{3+} (21%) compared to VO^{2+} (12%) was observed so that the conductivity loss by more absorption (or ion–exchange) of vanadium ion is more critical reason for the conductivity loss.

The *ex-situ* membrane data were obtained at equilibrium between water and vapor. Thus, the data for RH < 95% may be useful for gas phase batteries or PEMFCs. Note that we extrapolated all the conductivity data to RH = 100% from 93%, and this conductivity will be critical for a VRFB (liquid phase). For this 100% RH extrapolated value, Table 3 shows that the 242 mS cm^{-1} membrane conductivity for the pristine NRE211 decreased by 30 and 20 mS cm^{-1} for the 12% of VO^{2+}- and 21% of V^{3+}-exchanged NRE211s, respectively, which was an order of magnitude difference.

Li et al. [15] reported that *ex-situ* membrane conductivity for Co^{2+} absorbed to NRE211 decreased from 272 to 32 mS cm^{-1}at RH = 100% and T = 80 °C, which is consistent with Table 3. These authors assumed that the NRE211 membrane was fully exchanged with Co^{2+}, however, these authors did not measure the % absorbed for Co^{2+}. Kelly et al. [13,14] also reported the loss of membrane conductivity (N117) from 77 to 2 mS cm^{-1} after full exchange with Fe^{3+}. In summary, vanadium absorption to Nafion® membranes leads to a significant loss of conductivity even though less

Table 3
Comparison of membrane conductivity of N115 with VO^{2+} (V^{4+}), V^{3+}, Na^+, and Ca^{2+}.

Pristine		Na^+ (99%)		Ca^{2+} (40%)		V^{3+} (21%)		VO^{2+} (12%)	
RH [%]	σ [mS cm^{-1}]	RH [%]	σ [mS cm^{-1}]	RH [%]	σ [mS cm^{-1}]	RH [%]	σ [mS cm^{-1}]	RH [%]	σ [mS cm^{-1}]
22	7.39	22	0.16	20	0.016	22	0.00302	22	0.0252
31	14.1	30	0.537			31	0.0244	30	0.0931
41	23.7	39	0.856	40	0.1	41	0.125	39	0.343
50	36	49	2.35			50	0.437	49	1.02
61	51.9	58	5	60	0.76	61	1.18	58	2.32
68	68.2	67	7.52			68	2.47	67	4.19
82	104	80	16	80	3.4	82	5.87	80	9.22
88	130	85	21.7			88	8.47	85	12.7
93	170	92	31.3	95	18	93	12.6	92	19.8
100	[a]242	100	[a]72	100	[a]26	100	[a]20	100	[a]30

[a] Extrapolation value from a linear relation between logσ and RH (i.e., logσ = aRH + b, where a and b are constants).

absorption (or exchange) occurred. Note that Kelly et al. [13] also reported less absorption of Fe^{3+} on N117. Additionally, the conductivity loss in these experiments was greater than the loss observed at the same % of exchange for the absorption of alkali metals such as Na^{+} and Ca^{2+}.

4. Conclusions

In this paper, the ion–exchange/absorption behavior of vanadium in Nafion® membranes and the corresponding conductivity loss were studied. The maximum loss of IEC was measured to be less than 32% for all four oxidation states of vanadium. Additionally, the affinity of the vanadium ions to Nafion® showed the highest affinity (32%) for the lowest valence, V^{2+}, and lowest affinity (3%) for highest valence, VO_2^{+} (V^{5+}). The low % exchange and the valence effect can be explained by either the Donnan potential or the steric (or sieve) effect. The absorption isotherm did not change for different concentrations of V^{3+} (i.e., similar to Na^{+}), and we do not expect concentration to effect this process. Finally, the *ex-situ* membrane conductivity for vanadium-exchanged NRE211 (i.e., 12% of VO^{2+} and 21% of V^{3+}) was 2-3X lower than the conductivity of Na^{+}-exchanged (i.e., ≥99%) membranes at RH = 100%, but this value was similar to the Ca^{2+}-exchanged membrane (i.e., 60%). Thus, an order of magnitude loss of membrane conductivity in a VRFB is expected compared to pristine Nafion®.

Acknowledgments

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Appendix A

Table A1
Raw data for vanadium absorption measurement by AA, and UV–vis (shown in Fig. 1).

Species	pH	Concentration [N]		The ionic fraction of vanadium in acid solution	The measured amount of vanadium in N115 [μmol]	Equivalent vanadium in N115 [μmol]	The ionic fraction of vanadium in N115
		V	H_2SO_4				
VCl (s)/V^{2+}	2.35–2.90	0.027	0.240	0.10	14	28	0.16
		0.086	0.200	0.30	30	60	0.33
		0.151	0.151	0.50	29	58	0.32
		0.233	0.100	0.70	31	62	0.34
		0.451	0.050	0.90	29	58	0.32
V_2O_3 (s)/V^{3+}	1.04–2.00	0.01	0.09	0.09	4	12	0.06
		0.03	0.07	0.30	12	36	0.17
		0.05	0.05	0.50	15	45	0.22
		0.075	0.025	0.75	16	48	0.28
		0.09	0.01	0.90	16	48	0.29
$VOSO_4$ (aq)/VO^{2+}	1.1–2.7	0.4	3.6	0.10	4	9	0.05
		1.2	2.8	0.30	7	14	0.07
		2.0	2.0	0.50	9	18	0.09
		2.8	1.2	0.70	10	20	0.10
		3.6	0.4	0.90	12	24	0.12
V_2O_5 (s)/VO_2^{+}	−0.28–0.07	0.005	4.395	0.001	1	1	0.01
		0.22	4.18	0.05	4	4	0.02
		0.7	3.7	0.16	4	4	0.03
		0.9	3.5	0.21	5	5	0.03

Capacity of N115 sample = 180 μmol.

Table A.2
Raw data for vanadium absorption measurement by AA, and UV–vis (shown in Fig. 2).

Species	pH	Concentration [N]		The ionic fraction of vanadium in acid solution	The measured amount of vanadium in N115 [μmol]	Equivalent vanadium in N115 [μmol]	The ionic fraction of vanadium in N115
		V	H_2SO_4				
V_2O_3 (s)	1.34–2.30	0.009	0.091	0.09	5	15	0.08
		0.015	0.085	0.15	7	21	0.12
		0.03	0.07	0.3	10	30	0.17
		0.050	0.05	0.5	13	39	0.22
	1.04–2.00	0.01	0.09	0.09	4	12	0.06
		0.03	0.07	0.30	12	36	0.17
		0.05	0.05	0.50	15	45	0.22
		0.075	0.025	0.75	16	48	0.28
		0.09	0.01	0.90	17	51	0.29
	−0.27–0.30	0.3	3.7	0.08	1	3	0.02
		0.6	3.4	0.15	4	12	0.06
		1.2	2.8	0.3	7	21	0.12
		2.4	1.6	0.6	14	42	0.23
		3.0	1.0	0.75	17	51	0.28

Capacity of N115 sample = 180 μmol.

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